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COMPLETE SPECIFICATION

Improvements in or relating to the production of Polymers

We, DYNAMIT-ACTIEN-GESELLSCHAFT vormals Alfred Nobel & Co., a German Company of Troisdorf (22c), Nr. Cologne, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of polymers.

To the numerous compounds capable of polymerisation, there have recently been added, in addition to the ketone acetals of open structure, the dioxolanes having semi-cyclic double linkages, which, like the first-mentioned class of substances, and to some extent similarly to the vinyl and cyclic ethers, combine to form structures of higher molecular weight mainly in accordance with the principle of the ion chain polymerisation. The representatives of the dioxolane series capable of polymerisation include 4-methylene-, 2-propyl-4-methylene-, 2-vinyl-4-methylene-, 2-phenyl-4-methylene- and finally 4-methylene-5-methyl-1:3-dioxolane, such as are described in British Patent Specification No. 620,842.

The term "semi-cyclic double linkage" is used by analogy with the use of that expression by E. H. Rodd in "Chemistry of Carbon Compounds," Vol. II, page 145 (1st Edition, New York, 1953). Throughout this Specification and in the appended claims, the term is used to refer to a linkage in which one of the carbon atoms involved is part of a ring, whilst the other carbon atom is outside the ring.

It is also known that the said dioxolanes are capable of a mixed co-polymerisation with the usual vinyl compounds, including vinyl esters, vinyl halides, acrylic and methacrylic acid esters or divinyl compounds, such as butadiene, provided that a suitable catalyst is selected. In

any case, with regard to the dioxolanes, allowance must always be made for the fact that the polymerisation thereof, as mentioned, almost always takes place as an ion chain reaction, and consequently either responds badly or not at all to the usual polymerisation catalysts such as benzoyl peroxide or di-tert-butyl peroxide. (See J. Ab. Chem. Soc. 66, 1594 *et seq.* (1944) *ibid.* 72, 49 *et seq.* (1950)). Accordingly, in addition to boron fluoride and the complex compounds thereof, cadmium chloride and zinc chloride as well as tin tetrachloride, among others, have apparently proved suitable as polymerisation catalysts for the dioxolanes having semi-cyclic double linkages, such catalysts being employed, for example as far as zinc chloride is concerned, in quantities of 2—2.5%, calculated on the monomer. In such cases, the polymerisation is generally completed after about 18—24 hours. Unfortunately, however, the polymers obtainable in this manner, apart from the fact that the polymerisation takes a long time, are generally considerably coloured, while in addition their degree of polymerisation is generally rather low.

According to the present invention there is provided a process for the bulk polymerisation of dioxolanes having one or more semi-cyclic double linkages including the step of catalyzing the reaction with an addition compound of a polar solvent and a hydrohalide acid salt of a metal of the second or fourth group of the Periodic Table.

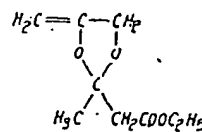
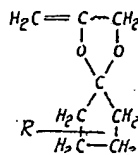
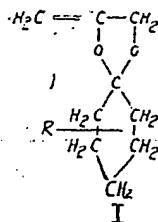
It is to be understood that throughout this Specification and in the appended claims the use of the term "polar solvent" is meant to include solvents having a partial dipole moment (but does not include water).

The process of the invention allows the polymerisation to be effected in a con-

siderably shorter time than heretofore and promotes the formation of substantially colourless, water-clear polymers.

- It is possible, *inter alia*, to carry out the polymerisation of cyclohexylidene acetal or methylcyclohexylidene acetal of propene (1)-diol (2:3) of the formula I, (R representing an optional alkyl

radical thereby to include the case of ketals of the alkyl homologues) and furthermore of the corresponding cyclopentylidene acetal (II) or finally of 3-methyl-4-methylene-1:3-dioxolane-2-acetic acid ethyl ester (III) in the presence of only 0.02 to 0.2% by weight



II

III

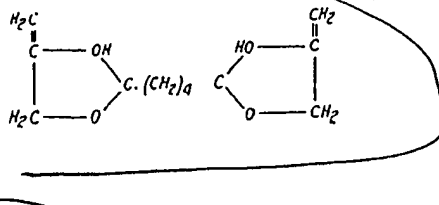
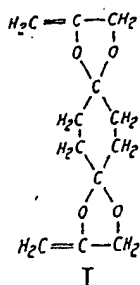
- of the complex compound of zinc chloride and methyl alcohol or ethyl alcohol (generally as 25% alcoholic solution) or of the analogous compounds of mercuric chloride or cadmium chloride within a few minutes. Alcoholic solutions of stannous chloride also behave similarly. Care must merely be taken to dissipate the liberated polymerisation heat in good time, since the temperature, if it is not kept within the necessary limits by external cooling, increases to 120°—130° C. within a few minutes after the addition of the catalyst, whereby slightly yellowish polymers or polymers permeated by blisters are obtained, especially with quantities of catalyst of more than 0.05%. Occasionally, and especially when the temperature of the monomer is below 15—20° C., the polymerisation has a great tendency to start slowly, but then rapidly speeds up as soon as the temperature of the monomer is brought to approximately 25°, up to a maximum of 28° C. On the other hand, if the conditions are so chosen that before the addition of the catalyst the monomer or mixture of monomers in question is preheated to 25—26° C. the polymerisation starts within a few seconds of the addition of the catalyst and, if the reaction temperature is maintained between 50° and 60° C., a completely clear, colourless and blister-free polymer is obtained. After one or at the most two hours, the polymerisation stops. Occasionally, depending upon the constitution of the monomer, however, the polymerisation slowly continues at room temperature; but even then it ends after about 8—10 hours.

Furthermore, it has been found desirable, in cases where it is desired to produce soft resins on the basis of such polymers to subject the said polymers to a

subsequent pressure hydrogenation in the presence of suitable solvents for the purpose of removing residual monomers. In any case, the by no means unpleasant odour which is sometimes peculiar to the polymers (due to traces of monomers), as well as the varying tendency to surface yellowing which may be observed, are thereby avoided. The polymers obtainable in this manner are very suitable as soft resins for lacquers having a nitro-cellulose base by reason of their excellent tolerance for nitro-cellulose, but they also give, as such, in suitable solvents, after drying, transparent, colourless and non-sticky lacquer films having good adhesive strength. Their solubility is excellent in almost all the usual organic solvents, including petroleum spirit, the only occasional exceptions being the lower alcohols, such as methanol and ethanol, depending upon the structure of the monomer. It has unexpectedly been found that an advantage is thereby obtained in that the addition of soft resins based on the said polydioxolanes also produces to some extent a stabilisation of the nitro-cellulose under the influence of light.

If, instead of dioxolanes having only one semi-cyclic double linkage, compounds are employed which contain several such groupings in the molecule, of which the compound I herein after reproduced by means of formula diagrams, namely cyclohexane dione (1:4)-bis-[propene (1)-diol (2:3)-acetal] or the 1:2- or 1:3-isomers thereof or the compound II, 1:4-bis-[2:2'-(4-methylene-1:3-dioxolyl)]-butane or di-[propene (1)-diol (2:3)-acetal] of adipic dialdehyde, or the corresponding diacetals of malonaldehyde, succinaldehyde or gluteraldehyde may be cited as examples.

completely cross-linked and consequently obtained under conditions similar to quick-hardening block polymers are those hereinbefore described.



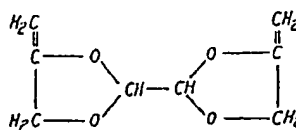
Like the non-cross-linked soft resins, these polymers are distinguished by complete transparency and lack of colour, and generally also by lack of odour. It has in addition been found particularly advantageous to subject the last-mentioned dioxolanes, i.e., those characterised by two semicyclic double linkages to a mixed copolymerization with the above mentioned monomers only containing one active group in the molecule, in which case only a small proportion of the doubly unsaturated compound, generally up to a maximum of 25% by weight calculated on the mixture of monomers, is sufficient to produce completely hardened, blister-free and glass-clear products. For the mixed copolymerisation at the most 0.05% of catalyst (as alcoholic solution) is here again sufficient, while the temperature should also not exceed 60° C. and must therefore again be moderated in each case by cooling in order to avoid the formation of blisters. Naturally, variable degrees of softness or hardness can be obtained by modifying the proportions of the two polymerisation components or of a triple mixture.

If monomers still contain polar groups, such as chlorine, cyanogen or carboalkoxy groups, in the molecule are selected as reaction components, the proportion of doubly unsaturated compounds as cross-linking component can be further reduced because the degrees of hardness of the mixed polymer which can thus be obtained are determined by factors other than that of a pure cross-linking.

The products obtained are particularly suitable for the production of moulded articles, but they are also excellently suitable for other purposes, for example, for the production of quick-hardening lacquers, owing to their transparency and their surface gloss, coupled with a good adhesive strength on the most varied carrier materials.

In a further development of the invention, it has been found that, of the many

unsaturated dioxolanes whose structure is as aforesaid, bis-2:2'-(4-methylene-dioxolane), that is to say the bis-[propene (1)-(diol (2:3)-acetal)] of glyoxal having the structure shown below



which is technically easy to produce, leads to polymers with particularly valuable properties. The course of the polymerisation differs somewhat from that generally described above in that, while the same or substantially the same quantities of catalyst are employed, the heat of reaction is smaller and the rate of polymerisation is also somewhat reduced. However, it has the advantage that the polymerisation can be easily conducted from the technical viewpoint, because no external cooling is required to dissipate the heat of polymerisation. It has even been found desirable, after the main reaction has died down, as indicated by the drop in temperature, which in any case, has scarcely risen above 40° C. to leave the polymers, which are already somewhat viscous, at a temperature of 40—50° C. for about 8 to 16 hours. After this time, a completely colourless, crystal-clear and very tough polymer is obtained, which is distinguished by great surface hardness.

Naturally, the bis-dioxolane of which the formula diagram has been given in the foregoing, may also be subjected to a mixed copolymerisation with other doubly unsaturated bis-dioxolanes, for example those already mentioned at the beginning, while the singly unsaturated dioxolanes may also be incorporated in any desired proportions. However, if it is desired to produce completely hardened polymers, the proportion of singly unsaturated components should not be too

high, and in any case should not exceed 50% by weight, since in this case the surface hardness of the mixed polymer would be unsatisfactory.

- 5 A content of from 5% up to a maximum of 25% of monomer calculated on the doubly unsaturated compound introduced has been found particularly suitable, because it has to some extent an elasticising action. In cases where greater importance is attached to the production of soft, crystal-clear lacquers or other transparent, more or less plasticised coatings, the content of singly unsaturated polymerisation component may be increased to 70% or 80%, since even with this proportion a sufficient hardness is ensured by the cross-linking component, depending upon the purpose of use. Here again, even in the case of corresponding triple mixtures, however, the polymerisation conditions are substantially the same, especially as regards the type and quantity of catalyst. It must, however, be borne in mind that as the content of singly unsaturated monomers increases, the heat of polymerisation rises accordingly, so that care must be taken to ensure that the heat is dissipated in good time by external cooling at least at the start of the reaction.

- 10 The contraction in the polymerisation is about 10%, corresponding to a ratio of 1:1.1 of the density of the monomer to that of the polymer. These figures naturally only apply in cases where the doubly unsaturated propene-diol acetal of the glyoxal is employed as such in the polymerisation, while in the case of mixtures of monomers the contraction, as a function of the density ratio, is naturally somewhat different.

- 15 If colouring of the polymers is desired, this is possible provided that non-basic colouring substances of suitable solubility are employed, since the small quantities of catalyst scarcely affect the colour shade. However, it is desirable to add the colouring substance directly to the monomer, since subsequent colouring entails difficulties owing to increasing viscosity.

- 20 The invention is illustrated by the following Examples.

EXAMPLE I.

- 25 100 g. of propene (1:2:3)-cyclohexylidene acetal (colourless to slightly yellowish liquid—b.p.₁₀ 79–82° C.) are preheated to 25–28° C. and mixed with 0.2 cc. of an ethyl alcohol solution of zinc chloride (which contains 25 g. of ZnCl₂ in solution per 100 cc.) with stirring. After a short time, the liquid, the occasional yellow coloration of which disappears immediately upon addition of the first drop of the catalyst solution, com-

mences to cloud, this indicating the commencement of the polymerisation. The temperature rapidly rises within a few seconds or minutes (depending upon the purity of the monomer) and is maintained between 50° and 60° C. by periodic external cooling in ice water in order to produce a colourless polymer. The mixture is then left for a few hours at room temperature in order to complete the polymerization. A completely colourless, crystal-clear polymer is obtained, which cannot be poured at normal temperatures and which is very readily soluble in all usual organic solvents, with the exception of the lower alcohols, and, on drying of the solutions, leaves a transparent, highly glossy film which becomes non-sticky after a few seconds. In cases where the characteristic odour adhering to the polymer (due to fractions of monomer still present), which is by no means unpleasant and which is soon dispersed in a thin layer, is found undesirable, it is desirable to subject the product subsequently to a pressure-hydrogenation (in suitable solvent) until the hydrogen absorption is constant. In addition, this has the advantage that it removes the tendency of the polymers to turn yellow on the surface, which is often observed, especially with this particular unsaturated dioxolane, and which is due to traces of monomer, although this tendency scarcely occurs in thin layers.

If cadmium chloride, or mercuric chloride is employed instead of zinc chloride, the course of the polymerisation is substantially the same as hereinbefore described, except that, owing to the lower solubility of these salts in alcohol (methyl alcohol or ethyl alcohol) substantially more dilute solutions must be employed. Moreover, the polymerisation can be carried out in substantially the same way with a concentrated (about 25%) solution of zinc chloride in acetone.

EXAMPLE II.

100 g. of propene (1:2:3)-cyclopentylidene acetal, a colourless liquid of b.p.₁₀ = 63–65° C. and of terpene-like odour, are polymerised as described in I. The polymer differs in its properties from the aforesaid higher ring homologues, but possibly has a somewhat softer character.

EXAMPLE III.

25 g. of cyclohexane dione (1:4)-bis-[propene (1:2:3)-acetal], a colourless liquid of b.p.₁₀ 152–154° C. which immediately solidifies in the form of macroscopic silvery crystals having a fusion point of 97–99° C. are stirred in 75 g. of the dioxolane mentioned in I, until the whole has dissolved. After heating to 28–30°, 0.2 cc. of 25% alcoholic

zinc chloride solution is stirred in and the mixture is left until the temperature automatically begins to rise. Should this not happen, the preheating may be increased by a few degrees, or 0.1 cc. of the catalyst solution may again be added. A temporary slight turbidity is then immediately observed, which again indicates the commencement of the polymerisation. If the temperature is maintained constant at 50–60° C. (by occasional external cooling) to avoid blistering and local yellowing, there is obtained after the complete polymerisation (at room temperature) a water-clear, completely colourless polymer which cannot be intended by pressure and which sometimes exhibits stickiness on the surface owing to admission of air during the polymerisation, but can be well mechanically worked after the removal of this sticky layer.

EXAMPLE IV.

A mixture of 77 g. (0.5 mol.) of propene (1)-diol (2:3)-cyclohexylidene acetal and 56 g. (0.25 mol. = 50 mol. per cent., calculated on the singly unsaturated dioxolane) of the cyclohexane dione (1:4)-bis-[propene (1)-diol (2:3)-acetal] already mentioned in the foregoing is first pre-heated to 35–40° C. with stirring in order to effect a better solution of the bis-dioxolane. The temperature of the monomer mixture is then allowed to fall to 28–30° C. and 0.5 cc. of an acetone solution of zinc chloride (containing 25 g. of metallic salt in solution to 100 cc.) is stirred in. When the polymerisation has started, the temperature of the mixture is maintained at 50–60° C. with occasional further stirring in order to avoid crystallisation of the monomeric diene. The viscosity rapidly increases, during which the stirring must be stopped in good time to avoid blistering, and after the complete polymerisation (at room temperature) a colourless water-clear polymer is obtained, which differs from the product obtainable in accordance with Example 3 by greater hardness owing to more extensive cross-linking.

EXAMPLE V.

113 g. (0.5 mol.) of 1:4-bis-[2:2'-(4-methylene-1:3-dioxolyl)]-butane or di-[propene (1)-diol-(2:3)-acetal] of adipic dialdehyde, a colourless viscous liquid of b.p.₁₂ 155–157°, which gradually turns yellow under lengthy standing, are polymerised with periodic external cooling, while 0.25 cc. of an alcoholic zinc chloride solution of the concentration indicated in Example I is stirred in at a temperature not exceeding 60° C. A colourless, clear and very tough polymer is obtained.

EXAMPLE VI.

0.4 cc. of a 25% alcoholic zinc chloride solution (corresponding to 0.1%) is added drop-by-drop at room temperature to 100 g. of bis-2:2'-(4-methylene-dioxolane), which is a colourless to slightly yellow liquid of b.p.₁₂ 100–120° C. (d₄²⁰ = 1.209) and the mixture is then thoroughly stirred. If desired, occluded air may be driven off by blowing in oxygen-free nitrogen. The liquid is instantaneously decoloured (if it was initially yellow). After a few seconds a slight turbidity is observed, which rapidly increases and reaches its maximum in the course of from 3 to 4 minutes. The temperature at the same time rises to about 38–40° C. seldom higher, and remains at this level for some time (about 30 to 45 minutes). A temperature reversal then occurs with increasing clarification of the liquid. At about this stage, the polymer, which has meanwhile become extremely viscous, is placed in a heating compartment and the polymerisation is completed at 38–42° C. within 8 to 12 hours. If desired, the temperature may thereafter be increased for 1 to 2 hours to 60° C. There is thus obtained after removal from the mould a completely colourless water-clear polymer which can be ground and polished in the manner of glass by reason of its surface hardness, and its density which is 1.346.

EXAMPLE VII.

A mixture of 90 g. of the doubly unsaturated compounds mentioned in Example VI and 10 g. of cyclohexanone-propene (1)-diol (2:3)-ketal is polymerised as before with the addition of 0.4 cc. of a 25% alcoholic zinc chloride solution, the course of the reaction not differing substantially from that described in Example VI. Exactly the same treatment as that hereinbefore described is then applied, a crystal-clear, completely colourless polymer of great brilliance again being obtained, which may have a somewhat tougher character, but which can also be readily worked.

EXAMPLE VIII.

1.2 cc. of a 25% alcoholic zinc chloride solution are added at room temperature to a solution of 60 g. of cyclohexane-dione-1:4-bis-[propene (1)-diol (2:3)-ketal] in 240 g. of bis-2:2'-(4-methylene dioxolane), and the solution is well shaken or stirred to effect a uniform distribution of the catalyst.

If desired, after the addition of the catalyst, nitrogen may be blown through the solution to drive off the air, but this is not essential. After a few seconds, the solution begins to cloud and after about 3 to 5 minutes the turbidity has reached its maximum. The temperature rises at

the same time to a maximum of 40° to 45° C. and remains for some time at this level. Should it by way of exception rise above 50° C. (in the case of larger proportions), cooling must accordingly be effected. After about one-half to three-quarters of an hour, the turbidity has for the greater part disappeared, and the product is then kept for 3—5 more hours in a heating compartment at 40° C. in order to complete the polymerization. The polymer thus obtainable is a completely colourless, crystal-clear product which is distinguished from the polymers mentioned in Examples I and II by even greater surface hardness.

EXAMPLE IX.

100 g. of bis-2:2¹ - (4-methylene-dioxolane) are polymerised with an addition of 0.4 cc. of a 25% stannous chloride solution in absolute alcohol, as described in Example VI. The polymer thus obtainable scarcely differs from the product which can be obtained by means of alcoholic zinc chloride solution.

What we claim is:—

1. Process for the bulk polymerisation of dioxolanes having one or more semi-cyclic double linkages including the steps of catalyzing the reaction with an addition compound of a polar solvent and a hydrohalide acid salt of a metal of the second or fourth group of the Periodic Table.

2. Process as claimed in claim 1, wherein the dioxolane is selected from the group consisting of the cyclohexylidene acetal of propane (1)-diol (2:3), the methylcyclohexylidene acetal of propane (1)-diol (2:3) and 2-methyl-4-methylene-1:3-dioxolane-2-acetic acid ethyl ester.

3. Process as claimed in claim 1 or 2, wherein the polar solvent is an alcohol.

4. Process as claimed in any preceding claim, wherein the hydrohalide acid salt is zinc chloride or stannous chloride.

5. Process as claimed in claim 1, 2, or 3, wherein the polar solvent is ethyl alcohol and the acid salt is zinc chloride, mercuric chloride, cadmium chloride or stannous chloride.

6. Process as claimed in any preceding

claim, wherein the weight of catalyst lies between 0.02 and 0.2%.

7. Process as claimed in any preceding claim, wherein the polymer obtained is subjected to a subsequent pressure hydrogenation.

8. Process as claimed in any preceding claim, wherein the dioxolanes have a plurality of semi-cyclic double linkages.

9. Process as claimed in claim 8, wherein the dioxolanes are selected from the group consisting of cyclohexanediones - bis - [propene (1) - diol (2:3)-acetals], 1:4-bis-[2:2¹-(4-methylene-1:3-dioxolyl)]-butane, or the di-[propene (1)-diol (2:3)-acetal] of adipic aldehyde, or of the corresponding diacetals of malonaldehyde, succinaldehyde, or glutaraldehyde.

10. Process as claimed in claim 8, wherein the dioxolane is the bis-[propene (1)-diol (2:3)-acetal] of glyoxal.

11. Process as claimed in any preceding claim, wherein a dioxolane having one semi-cycle double linkage is subjected to a mixed copolymerisation with a dioxolane having two semi-cyclic double linkages.

12. Process as claimed in any preceding claim, wherein the dioxolanes contain polar groups such as chlorine, cyanogen or carboalkoxy groups.

13. Process as claimed in claim 10, wherein the bis-[propene (1)-diol (2:3)-acetal] of glyoxal is subjected to a mixed copolymerisation with another dioxolane having two semi-cyclic double linkages and a dioxolane having one semi-cyclic double linkage.

14. Process for the polymerisation of dioxolanes substantially as hereinbefore described with reference to any of the specific Examples.

15. Polymers produced by the process claimed in any of the preceding claims.

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